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(54) TITLE OF THE INVENTION

A method of manufacturing 1,4-butanediol and tetrahydrofuran.

(57) [SCOPE OF CLAIM]

[Claim 1] A method of manufacturing 1,4-butanediol and tetrahydrofuran, characterized in that maleic anhydride and/or succinic anhydride are catalytically hydrogenated

in the vapour phase in the presence of a solid catalyst containing copper and aluminium.

#### [DETAILED DESCRIPTION OF THE INVENTION]

##### Field of Industrial Use

The invention relates to a method of manufacturing 1,4-butanediol and tetrahydrofuran; in further detail it relates to a method of manufacturing 1,4-butanediol and tetrahydrofuran, by hydrogenating maleic anhydride and/or succinic anhydride in the vapour phase in the presence of a catalyst.

##### Prior Art

1,4-butanediol is a compound which is useful as a raw material for manufacturing polybutylene terephthalate resins, polyurethane resins and the like. It is therefore very desirable to develop a method of manufacturing 1,4-butanediol which is cheap and efficient.

The following methods of manufacturing  $\gamma$ -butyrolactone and 1,4-butanediol by catalytic hydrogenation of maleic anhydride and/or succinic anhydride or their derivatives have been disclosed in previous publications:

- (a) A method of manufacturing  $\gamma$ -butyrolactone by hydrogenation of maleic anhydride, succinic acid or the like in the vapour phase using a catalyst containing zinc, copper and chromium (JAPANESE EXAMINED PATENT 44-32567).
- (b) A method of manufacturing  $\gamma$ -butyrolactone by hydrogenation of maleic anhydride and/or succinic

acid in the vapour phase in the presence of a copper oxide - beryllium oxide - zinc oxide reduction catalyst (JAPANESE EXAMINED PATENT 47-23294).

- (c) A method of manufacturing 1,4-butanediol by hydrogenation of maleic anhydride or succinic anhydride in the liquid phase in the presence of a catalyst containing a Subgroup VII or Subgroup VIII element or compound (JAPANESE UNEXAMINED PATENT 51-133212).
- (d) Methods for manufacturing 1,4-butanediol by hydrogenolysis of maleic acid diesters or fumaric acid diesters, in the vapour phase in the presence of a copper chromite catalyst (JAPANESE UNEXAMINED PATENT 61-22035 and JAPANESE PATENT PUBLICATION (PCT) Number 62-501702).

The authors have also put forward a method for manufacturing 1,4-butanediol, which is carried out by hydrogenating maleic anhydride and/or succinic anhydride in the vapour phase in the presence of a copper oxide - zinc oxide catalyst (JAPANESE PATENT APPLICATION 63-175062).

Tetrahydrofuran is also useful as a raw material for polytetramethylene glycol and the like and as a solvent for poly(vinyl chloride), polyurethane and the like and it is desirable to develop a cheap and efficient method for manufacturing it, together with 1,4-butanediol.

The following methods of manufacturing tetrahydrofuran by catalytic hydrogenation of maleic anhydride and/or succinic anhydride or the like have been disclosed in previous publications:

- (a) A method of manufacturing tetrahydrofuran by hydrogenating and dehydrating maleic anhydride and/or succinic anhydride and/or  $\gamma$ -butyrolactone or the like in the vapour phase in the presence of a mixture of copper-based catalyst and a dehydration catalyst (JAPANESE EXAMINED PATENT 48-30272).
- (b) Methods of manufacturing  $\gamma$ -butyrolactone and/or tetrahydrofuran by hydrogenation of maleic anhydride or succinic anhydride, or the like in the liquid phase in the presence of a solid catalyst containing palladium, cobalt and niobium (JAPANESE UNEXAMINED PATENT 62-111975).

The authors have also put forward a method for manufacturing tetrahydrofuran and 1,4-butanediol, which is carried out by hydrogenating maleic anhydride and/or succinic anhydride in the presence of a solid catalyst containing copper, chromium and manganese (JAPANESE PATENT APPLICATION 63-313760).

#### Problems to be Resolved by the Invention

However, the aforementioned methods disclosed for manufacturing 1,4-butanediol have the following problems. That is, with the exception of the method put forward by the inventors, there is the problem in methods of hydrogenating maleic anhydride and/or succinic anhydride in the vapour phase in the presence of a catalyst, that only  $\gamma$ -butyrolactone is formed and none of the intended 1,4-butanediol is obtained. There are also the problems in methods for hydrogenating maleic

anhydride and/or succinic anhydride in the liquid phase in the presence of a catalyst that the pressure required is high, approximately  $200 \text{ kg/cm}^2$ , so that extensive installation and operating costs are required. In methods for the hydrogenolysis of diesters of maleic acid in the vapour phase in the presence of a catalyst, although high pressure, as in the aforementioned methods, is not required, it is necessary to have a stage in which maleic anhydride is formed into one of its diesters; the processes required are thus very complex. That is, since the reaction to form a diester is an equilibrium reaction, it is necessary to have a two-stage reaction process, so that the reaction will proceed to a sufficient degree, and it is therefore necessary to add three additional reaction stages, when the monoester formation stage is included.

The aforementioned methods disclosed for manufacturing tetrahydrofuran have the following problems. That is, in the method of manufacturing tetrahydrofuran by hydrogenation and dehydration of maleic anhydride or the like, in the presence of a mixture of a copper-based catalyst and a dehydration catalyst, there are the problems that, since hydrogenation and dehydration need to be carried out with a division into three reaction zones, the reaction equipment and the processes are complex. Since methods for manufacturing tetrahydrofuran using catalysts containing palladium, cobalt and niobium are carried out in the liquid phase, there are also problems in respect of the requirements for high pressures and of the large quantities of  $\gamma$ -butyrolactone by-product which are formed.

In addition, no existing methods are known for jointly manufacturing 1,4-butanediol and tetrahydrofuran by catalytic hydrogenation of maleic anhydride and/or succinic anhydride in the vapour phase, apart from the method already put forward by the authors.

The invention is such that it resolves the problems accompanying existing methods of manufacture that there are high installation and operating costs and complex processes when 1,4-butanediol and tetrahydrofuran are manufactured from maleic anhydride and/or succinic anhydride; the invention is aimed at providing a method of jointly manufacturing 1,4-butanediol and tetrahydrofuran cheaply and efficiently.

#### The Means of Resolving the Problems

##### *Summary of the Invention*

The inventors considered that, if it would be possible to manufacture 1,4-butanediol and tetrahydrofuran by carrying out direct hydrogenation of maleic anhydride and/or succinic anhydride at low pressure, this would have great merit and they therefore investigated vapour phase hydrogenation methods.

It was also considered that the fact that  $\gamma$ -butyrolactone was not obtained in existing vapour phase hydrogenations of maleic anhydride and/or succinic anhydride was because all the reactions were carried out with low hydrogen to raw material ratios and at approximately normal pressure. It was discovered that 1,4-butanediol and tetrahydrofuran can be jointly manufactured in high yields when the reaction is carried out, under a pressure in a range which can support a vapour

phase, with higher hydrogen to raw material ratios than hitherto; the invention was thus achieved.

That is, the invention relates to a method of manufacturing 1,4-butanediol and tetrahydrofuran, characterized in that, in the method of manufacturing 1,4-butanediol and tetrahydrofuran by catalytically hydrogenating maleic anhydride and/or succinic anhydride, the maleic anhydride and/or succinic anhydride are hydrogenated in the vapour phase in the presence of a solid catalyst containing copper and aluminium.

#### Catalysts

The catalysts used according to the invention are normally pre-reduced copper oxide and aluminium oxide catalysts. Such catalysts are manufactured by dissolving copper compounds, such as copper nitrate, and aluminium compounds, such as aluminium nitrate, in water, adding aqueous sodium carbonate solution dropwise until the solution is neutral, with heating and mixing by stirring, then collecting the solid obtained by filtration, drying it and forming it into the required shape using a moulding machine. Copper oxide - aluminium oxide catalysts are obtained by this manufacturing method.

The reduction of the catalysts according to the invention is carried out by treatment by circulating, for twenty-four hours, nitrogen gas containing 2% by volume of hydrogen at a gas hourly space velocity calculated at normal temperature and normal pressure (G.H.S.V.) of 2400 per hour (all the G.H.S.V.'s below are expressed in terms of normal temperature and normal pressure), at an

applied pressure of a few tens of kg/cm<sup>2</sup> and at 170°C, after which the hydrogen concentration is gradually raised to 100% by volume and circulated through the catalyst bed at 200°C for a few hours.

#### Solvents

The solvents which may be used according to the invention are not especially restricted and examples of the solvents which may be used are:  $\gamma$ -butyrolactone, tetrahydrofuran, dimethyl ether, diethyl ether and 1,4-dioxan. Of these, since  $\gamma$ -butyrolactone is a good solvent for, and is a hydrogenation product of, maleic anhydride and/or succinic anhydride and is believed to be an intermediate for 1,4-butanediol, it is particularly preferred. It is also possible to use no solvent.

#### Catalysis Conditions

The method for bringing the gaseous mixture of maleic anhydride and/or succinic anhydride and hydrogen into contact with the catalyst may be selected as appropriate from amongst existing known methods. Examples of the methods which may be adopted for bringing the gaseous mixture into contact with a catalyst are contact by means of a fixed, moving or fluidized bed. The gaseous mixture may also be brought into contact with the catalyst in batch mode, if required.

The contact time between the gaseous mixture of maleic anhydride and/or succinic anhydride and hydrogen is an approximate G.H.S.V. of 1000 to 100,000 per hour, preferably 1500 to 20,000 per hour.



According to the invention, the reaction temperature is from approximately 170° to 280°C; the reaction pressure is from approximately 10 to 100 kg/cm<sup>2</sup> and the molar ratio of hydrogen to the maleic anhydride and/or succinic anhydride is from 50:1 to 1500:1. The reaction temperature, reaction pressure and molar ratio of hydrogen to the raw materials may be selected as appropriate to be within a range in which the vapour phase can be maintained.

However, if the molar ratio of hydrogen to the raw materials is less than 50, the rate of reaction falls and deterioration of the catalysts readily occurs, due to the formation of carbonaceous material, while, on the other hand if the molar ratio exceeds 1500, there is the economic disadvantage that large volumes of hydrogen must be recycled: neither of these situations is preferred.

The ratio of 1,4-butanediol to tetrahydrofuran in the product according to the invention varies depending on the reaction pressure and reaction temperature: it is generally within the molar ratio range, tetrahydrofuran to 1,4-butanediol = 1:3 to 100:0.

After finishing a reaction, 1,4-butanediol and tetrahydrofuran may be readily separated from the reaction mixture by known methods such as distillation.

#### Effects of the Invention

1,4-butanediol and tetrahydrofuran may be obtained from maleic anhydride and/or succinic acid in high yields in one step by using the method according to the invention

and this method of manufacturing can be made extremely simple. Furthermore, since the method of manufacturing 1,4-butanediol and tetrahydrofuran is carried out at far lower pressures than with liquid phase hydrogenation technology, the effect is obtained that installation and operating costs may be reduced.

The invention will be explained below by means of Examples of its execution, without the invention being limited by these Examples.

#### Example 1

A commercial copper-aluminium oxide catalyst [Trade Name E20K2, Nikki Kagaku K. K. (Nikki Chemical Company Limited), 15 cc] containing 36.7% by weight copper and 17.7% by weight aluminium (as copper and aluminium metals) was packed into a fixed bed reactor (15 mm diameter x 600 mm length) and heated to 170°C in a current of nitrogen at 40 kg/cm<sup>2</sup>G. After this, hydrogen was gradually added in a current of nitrogen and nitrogen gas containing 2% by volume of hydrogen was passed through for one night at 40 kg/cm<sup>2</sup>G, 170°C and G.H.S.V. 2400 per hour. The hydrogen concentration was further gradually increased to make the concentration 100% by volume, taking care that the catalyst bed temperature did not exceed 200°C, and reduction treatment was carried out at 40 kg/cm<sup>2</sup>G, 200°C, G.H.S.V. 2400 per hour for 2 hours.

The aforementioned fixed bed reactor was heated to a temperature of 230°C, after which a  $\gamma$ -butyrolactone solution of maleic anhydride (molar ratio of maleic anhydride to  $\gamma$ -butyrolactone, 1:1) and hydrogen gas, in

the proportion 200 parts per mole of maleic anhydride plus  $\gamma$ -butyrolactone, was circulated under the conditions, a pressure of 40 kg/cm<sup>2</sup>G and a G.H.S.V. of 9600 per hour. The products were analyzed by means of gas chromatography, identification being carried out by means of GC-MS.

The results were that the maleic anhydride conversion was 100% and 15.2 mole% 1,4-butanediol, 82.9 mole% tetrahydrofuran and 1.0 mole% n-butanol were formed per mole of maleic anhydride supplied. Traces of products other than n-butanol were formed, but no succinic anhydride was detected amongst the products.

#### Example 2

The treatment to reduce the catalyst and the reaction were carried out in a similar manner to Example 1, with the exceptions that the pressure during the reduction treatment and the reaction was 15 kg/cm<sup>2</sup>G, the reaction temperature was 210°C, the molar ratio of maleic anhydride to  $\gamma$ -butyrolactone was 1:3 and the G.H.S.V. was 3200 per hour.

The results were that the maleic anhydride conversion was 100% and 14.8 mole% 1,4-butanediol, 63.0 mole% tetrahydrofuran and 2.6 mole% n-butanol were formed per mole of maleic anhydride supplied. No succinic anhydride was detected amongst the products.

#### EXAMPLE 3

Copper nitrate [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 48.32 g] and aluminium nitrate [Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 150.05 g] were dissolved in water

(600 ml). To this solution was added dropwise, with stirring, a 1 mole/l aqueous solution of sodium carbonate, maintaining the temperature at 70° to 75°C, until the pH of the solution was 7.3, after which stirring was continued for 90 minutes, maintaining the temperature at approximately 80°C. The solution was allowed to cool, after which the solid which had formed was filtered off and rinsed through, using hot water (60°C, approximately 10 l). After this, the solid was dried in a current of air at 120°C and baked at 400°C for 3 hours, when 34 g of solid were obtained. This solid was moulded and powdered, after which it was graded to 6 to 10 mesh, when a solid catalyst comprising copper oxide and aluminium oxide was obtained. The amounts of copper and aluminium in the catalyst obtained, as metals, were, respectively, 28.5% by weight and 24.5% by weight.

Reduction treatment of the catalyst and reaction were carried out in a similar manner to Example 2, using 15 c.c. of the catalyst manufactured as above.

The results were that the maleic anhydride conversion was 100% and 0.2 mole% 1,4-butanediol, 99.1 mole% tetrahydrofuran and 0.7 mole% n-butanol were formed per mole of maleic anhydride supplied. No succinic anhydride was detected amongst the products.

#### Example 4

When treatment to reduce the catalyst and the reaction were carried out in an approximately similar manner to Example 2, with the exception that succinic anhydride was used instead of maleic anhydride, the reaction

product was approximately similar to that obtained in Example 2.

#### Example 5

Using some of the reduced catalyst used in Example 1, a solution of maleic anhydride in 1,4-dioxan (molar ratio of maleic anhydride to 1,4-dioxan = 1:3) and hydrogen, in the proportion 800 moles per mole of maleic anhydride were circulated through the reactor under the conditions, 210°C, a pressure of 15 kg/cm<sup>2</sup>G and a G.H.S.V. of 3500 per hour.

The results were that the maleic anhydride conversion was 100% and 3.8 mole% 1,4-butanediol, 81.6 mole% tetrahydrofuran and 14.1 mole% of  $\gamma$ -butyrolactone were formed per mole of maleic anhydride supplied. No succinic anhydride was detected amongst the products.

#### Example 6

Using some of the reduced catalyst used in Example 3, but no solvent, a mixture of maleic anhydride and hydrogen, in the proportion (molar ratio 1:600) was circulated under the conditions, 220°C, a pressure of 60 kg/cm<sup>2</sup>G and a G.H.S.V. of 4800 per hour.

The results were that the maleic anhydride conversion was 100% and 20.4 mole% 1,4-butanediol and 76.3 mole% tetrahydrofuran were formed per mole of maleic anhydride supplied. No succinic anhydride was detected amongst the products.

#### Example 7

The treatment to reduce the catalyst and the reaction were carried out in a similar manner to Example 1, with the exceptions that a solution of maleic anhydride and succinic anhydride in  $\gamma$ -butyrolactone (molar ratio of maleic anhydride to succinic anhydride to  $\gamma$ -butyrolactone = 3:1:4) was used instead of the  $\gamma$ -butyrolactone solution of maleic anhydride and the proportion of hydrogen which was circulated was 200 moles per mole of maleic anhydride plus succinic anhydride plus  $\gamma$ -butyrolactone.

The results were that the conversion of the maleic anhydride and succinic anhydride was 100% and 17.0 mole% 1,4-butanediol, 81.7 mole% tetrahydrofuran and 1.0 mole% n-butanol were formed per mole of maleic anhydride plus succinic anhydride supplied.